MD of liquid Lithium sputtering by He$^+$ ions and bubble formation

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Outline

- **MD study of diffusion in liquid Li and He/Li mixtures**

- **MD study of the Li sputtering Yields and He reflection coefficients for He+ ion collisions with a liquid He/Li surface**

- **He Bubble formation in liquid Li – MD, MC studies, existing problems and future work**

Molecular Dynamics method

MD numerically calculates the classical equations of motion (EOM) on a computer i.e. it gives the phase space trajectories of a system.

$$\overline{A} = \lim_{t' \to \infty} \frac{1}{(t' - t_0)} \int_{t_0}^{t'} A(r^N(t), p^N(t); V(t)) dt,$$

$$\overline{A} = \langle A \rangle_{NVE}.$$

The physical variables could be obtained by averaging over the trajectories. E.g., T and P are calculated as follows:
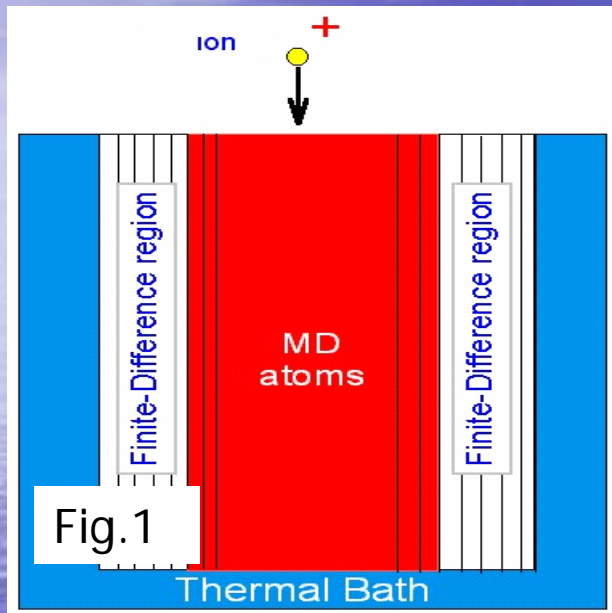
$$T = \langle T \rangle, \text{ where } T = \frac{2}{3k_B T} \sum_{i=1}^{N} \frac{mv_i^2}{2}$$

$$P = \langle P \rangle - \frac{\rho^2}{6} \int_{r_{cut}}^{\infty} r \frac{\partial \phi}{\partial r} g(\vec{r}) d\vec{r} ,$$

$$P = \rho k_B T - \frac{\rho}{3N} \sum_{i} \sum_{j>i} r_{ij} \frac{\partial \phi(r_{ij})}{\partial r_{ij}}$$

Here, $\phi(r_{ij})$ is the inter-particle potential function, r is the average density, $g(\vec{r})$ – the pair-correlation function – the probability for two particles to be a distance r.

Accelerated MD

Fig.1

Fig.2

Our **hybrid MD method** combines atom. Molecular Dynamics (the red area in Fig.1) with a continuum mechanics (blue & white areas) equations solved by elasticity theory and thermodynamics.
The HMD method:
1. Demonstrates correct physics.
2. Accel. computing by a factor of 100.
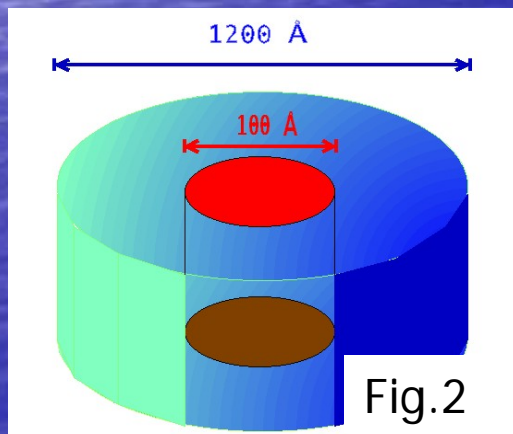3. Has little limitation for the system size.

Fig.2: a sample for solid surface study: the MD area (with extensive calculation load) is 100A in diameter but the total size of the effective size is 100 times bigger.
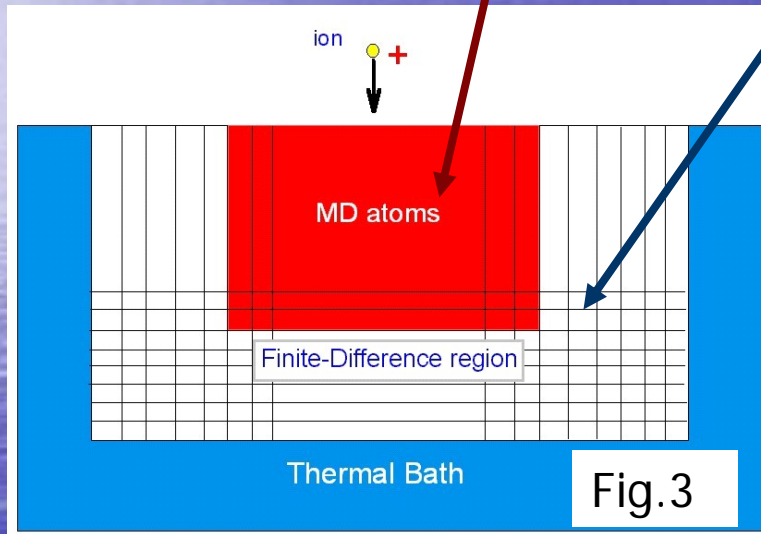
Concept for the Hybrid MD

The MD region :

$$\ddot{\vec{r}}_i(t) = -\frac{1}{m}\sum_{j \neq i}\frac{\partial U_{ij}}{\partial \vec{r}_{ij}}$$

ion $\bullet$ +

MD atoms

Finite-Difference region

Thermal Bath

Fig.3

The Finite - Difference Region (Mesh) :

Thermal balance :

$$\frac{dT(\vec{r},t)}{dt} = \chi \, \Delta T(\vec{r},t)$$

The eq. of motion :

$$\frac{d^2\vec{u}_i}{dt^2} = \frac{\partial \sigma_{ik}}{\partial x_k}$$

χ – thermal diffusivity,
K – bulk modulus,
ξ - bulk viscosity,
α – therm. expans coeff,
μ - shear modulus,
η - shear viscosity.

$$\sigma_{ik} = -\alpha K T \, \delta_{ik} + K \varepsilon_{ll}\delta_{ik} + 2\mu\left(\varepsilon_{ik} - \varepsilon_{ll}\frac{\delta_{ik}}{3}\right)$$

$$+ \xi\varepsilon_{ll}\delta_{ik} + 2\eta\left(\dot{\varepsilon}_{ik} - \dot{\varepsilon}_{ll}\frac{\delta_{ik}}{3}\right)$$

$$\varepsilon_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right)$$

Multi-scale Molecular Dynamics: Red area: MD region, the atomic equations of motion are solved (pink frame). Blue area: thermostat. White area – buffer between two regions.

Li-Li potential #1

TBQM (1) was used in [1] for obtaining a suitable ion-ion potential for disordered Lithium system (small clusters). He-He potential was chosen of a (exp-6) type [2]. Li-He potential was obtained by two ways: the Lorentz-Berthelot rule (#1) and from quantum mechanics [3].

$$(\varepsilon_{ia}^0 - E)\,|ia\rangle + \sum_{j \neq i}\sum_b t_{ab}^{ij}(r_{ij})\,|ib\rangle = 0, \quad (1)$$
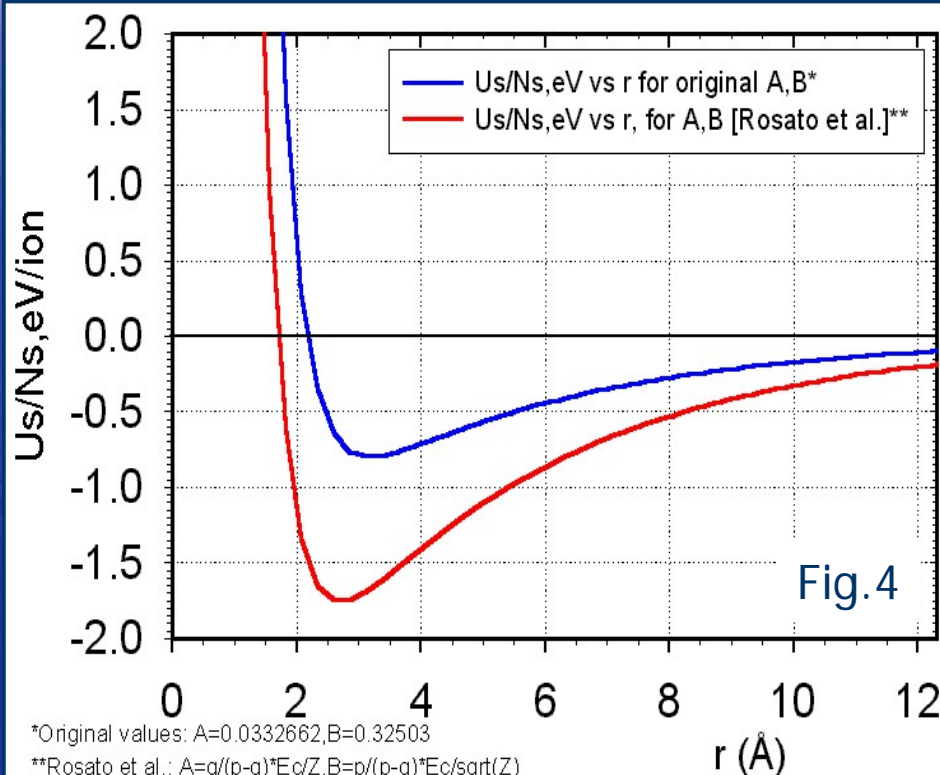
$$U_{coh} = U_{el} + U_{rep},$$

$$U_{rep} = \sum_i \varepsilon_0 \sum_{j \neq i} \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right],$$

$$U_{el} = -\sum_i \left\{ \sum_{j \neq i} \varsigma_0^2 \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right]\right\}^{1/2}$$

Parameters used for this simulation:

	ε_0, mRy	ς_0, mRy	p	q	r_0, a.u.
Li-Li:	2.4450	23.889	7.75	0.737	5.490
He-He:	0.0694		14.5		5.61
Li-He#1:	1.52		14.5		5.55
Li-He#2:	2.35				3.57

Fig.4

Legend:
— Us/Ns,eV vs r for original A,B*
— Us/Ns,eV vs r, for A,B [Rosato et al.]**

*Original values: A=0.0332662,B=0.32503
**Rosato et al.: A=q/(p-q)*Ec/Z,B=p/(p-q)*Ec/sqrt(Z)

Axis: Us/Ns,eV/ion vs r (Å)

Reference:
[1] Y. Li et al, Phys. Rev. B57 (1998) 15519.
[2] R.A. Aziz et al, JCP 94 (1991) 8047.
[3] P. Soldan, Chem.Rev.Lett. 343 (2001) 429.

Li-Li potential #2

In [1,2], a liquid Lithium potential was obtained and tabulated for five temperature and density points that are located near the Lithium experimental melting line [3]. We used cubic splines for energy and forces, to calculate the Li self-diffusion coefficient.
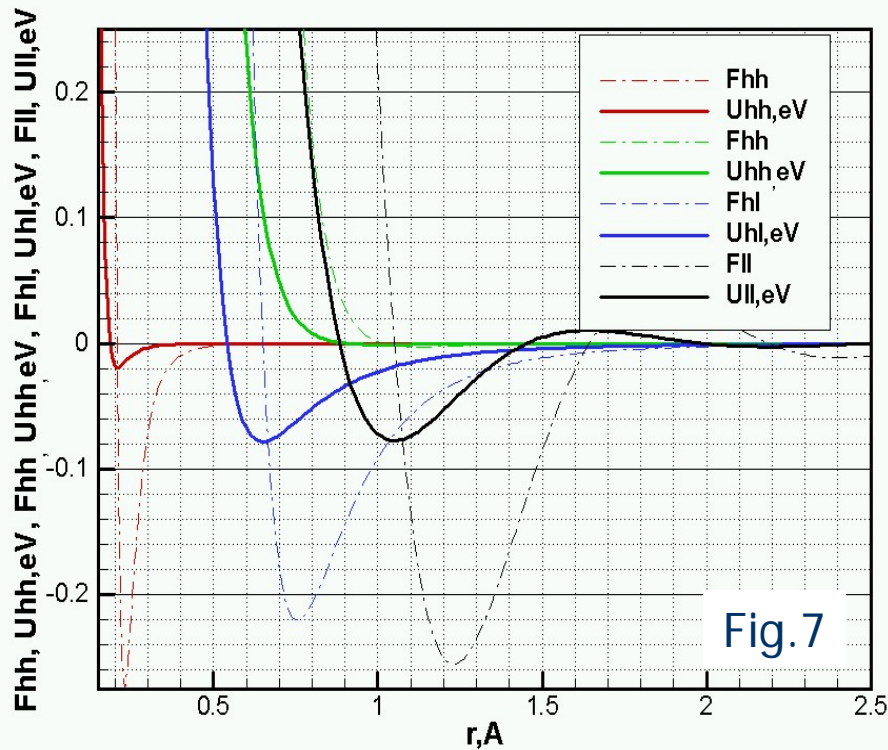

Fig.5

Fig.6
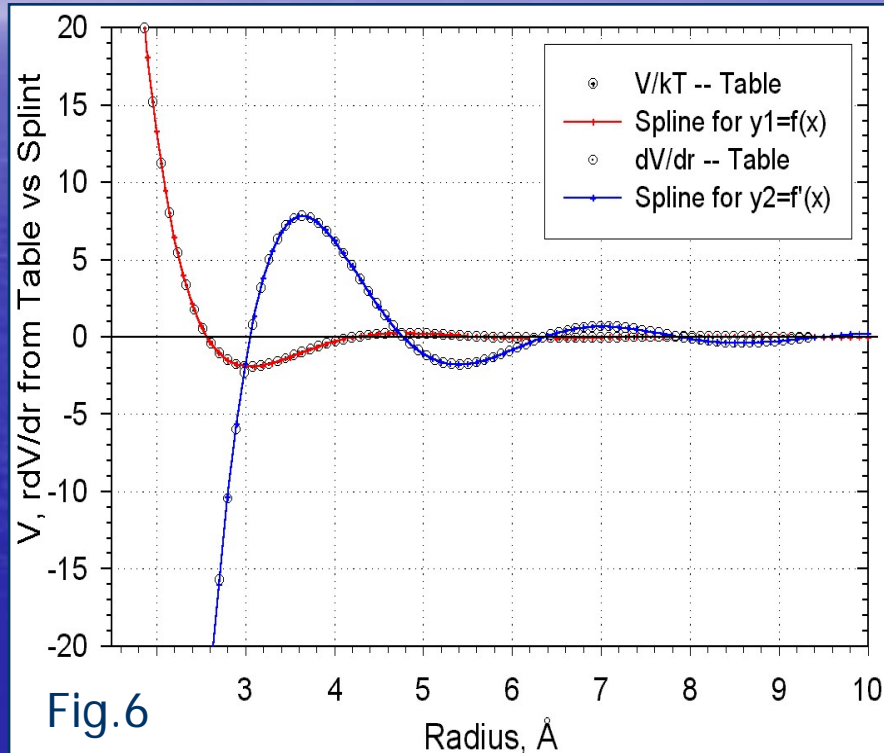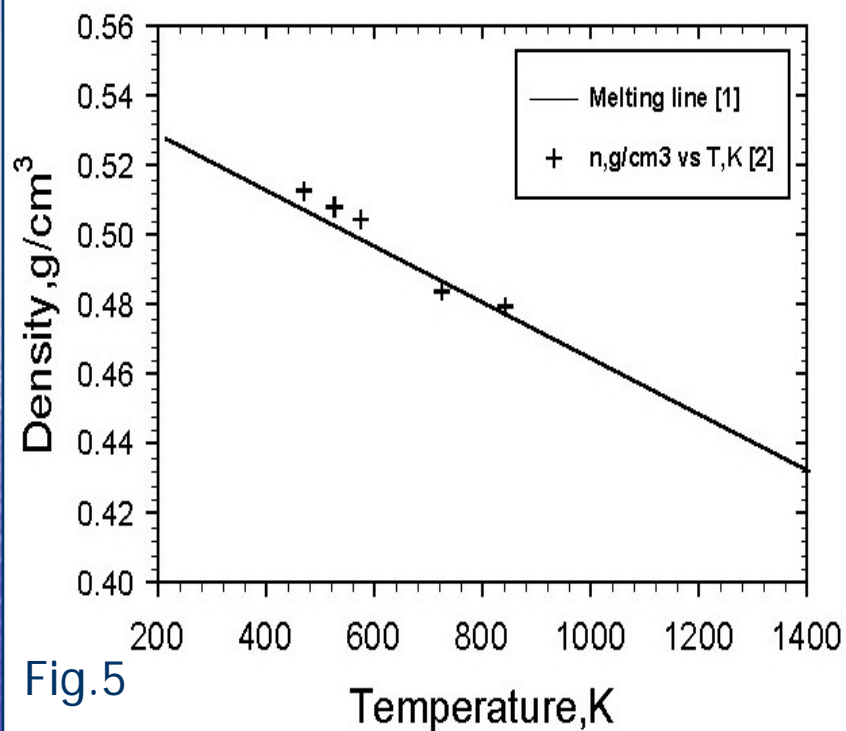
References:
[1] M. Canales et al, J. Phys. 5 (1993) 3095.
[2] M. Canales, Phys.Rev. E50 (1994) 3656.
[1] H. Morimoto et al, to be published.

The tabulated potential and its first derivative given in [1,2] (circles) and cubic splines (red and blue lines) used in this work.

He-Li potential

In [1], a He-Li potential function was obtained, as it is shown below.

Fig.7

Atomic units: Distance $a_0 = 0.529$Å, Energy $E_h = 27.2$eV,

References:
[1] P.Soldan et al., Chem.Rev.Lett. 343 (2001) 429-436.
[a] D.M. Bishop, J. Pipin, Chem.Rev.Lett. 236 (1995) 15.
[b] R.Ahlrichs, H.J. Böhm, S. Brode, K.T. Tang, J.P. Toennies, J. Chem.Phys. 88 (1988) 6290.

Evaluation of forces for the He-Li potential from Ref [1].

$$V_{rep}(R) = A\exp(-bR), \quad V_{atr}(R) = -\sum f_n(R)\frac{D_n}{R^n}, \quad (n=4,6,7,8)$$

$$f_n(R) = 1 - \exp(-bR)\sum_{k=0}^{n}\frac{[bR]^k}{k!},$$

$$A = 20.8682, \quad b = 2.554, \quad D_4 = \alpha_1/2, \quad D_6 = \alpha_2/2 + C_6, \quad D_7 = -B/2,$$

$$D_8 = \alpha_3/2 + \gamma/24 + C_8,$$

$$\alpha_1 = 1.383192^a, \quad \alpha_2 = 2.4451^a, \quad \alpha_3 = 10.6204^a, \quad \gamma = 43.104^a,$$

$$B = -7.3267^a, \quad C_6 = 0.298^b, \quad C_8 = 1.98^b.$$

$$F_r = -\frac{\partial V_{tot}}{\partial r} = -\left(\frac{\partial V_{rep}}{\partial r} + \frac{\partial V_{atr}}{\partial r}\right),$$

$$\left(\frac{\partial V_{rep}}{\partial r}\right) = -Abe^{-bR}.$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=4} = f_4'(R)\frac{D_4}{R^4} - 4f_4\frac{D_4}{R^5},$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=6} = f_6'(R)\frac{D_6}{R^6} - 6f_6\frac{D_6}{R^7},$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=7} = f_7'(R)\frac{D_7}{R^7} - 7f_7\frac{D_7}{R^8},$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=8} = f_8'(R)\frac{D_8}{R^8} - 8f_8\frac{D_8}{R^9}.$$

$$f_4(R) = 1 - e^{-bR}\left[1 + \frac{bR}{1!} + \frac{(bR)^2}{2!} + \frac{(bR)^3}{3!} + \frac{(bR)^4}{4!}\right],$$

$$f_6(R) = f_4(R) - e^{-bR}\left[\frac{(bR)^5}{5!} + \frac{(bR)^6}{6!}\right],$$

$$f_7(R) = f_6(R) - e^{-bR}\left[\frac{(bR)^7}{7!}\right],$$

$$f_8(R) = f_7(R) - e^{-bR}\left[\frac{(bR)^8}{8!}\right],$$

$$f_4'(R) = be^{-bR}\left[\frac{(bR)^4}{4!}\right],$$

$$f_6'(R) = f_4'(R) + be^{-bR}\left[\frac{(bR)^6}{6!} - \frac{(bR)^4}{4!}\right],$$

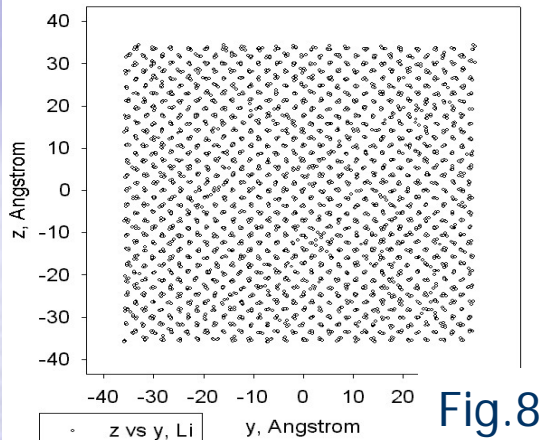$$f_7'(R) = f_6'(R) + be^{-bR}\left[\frac{(bR)^7}{7!} - \frac{(bR)^6}{6!}\right],$$

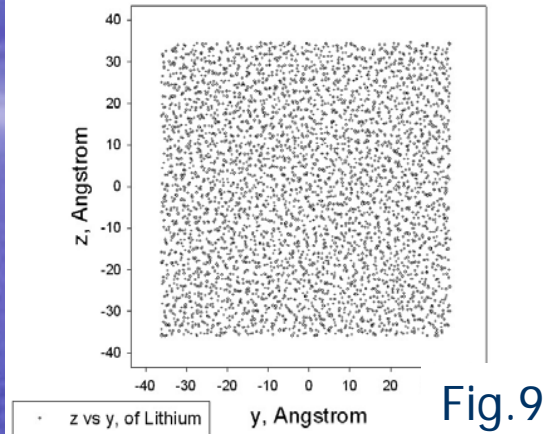$$f_8'(R) = f_7'(R) + be^{-bR}\left[\frac{(bR)^8}{8!} - \frac{(bR)^7}{7!}\right],$$

Melting of bulk Lithium

Lithium positions at t/dt=1000, density 0.508g/cm3,T=258K

Fig.8

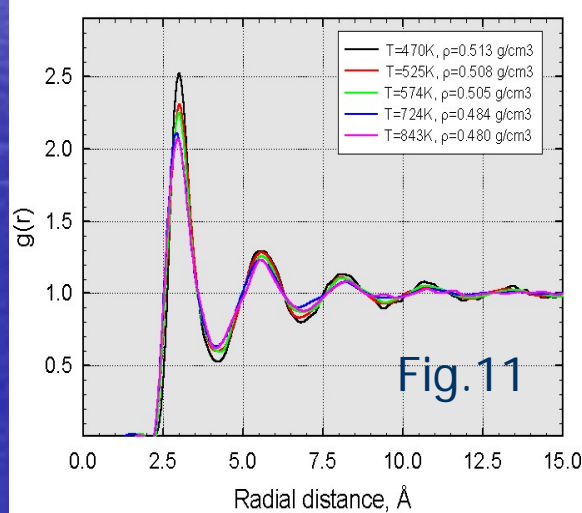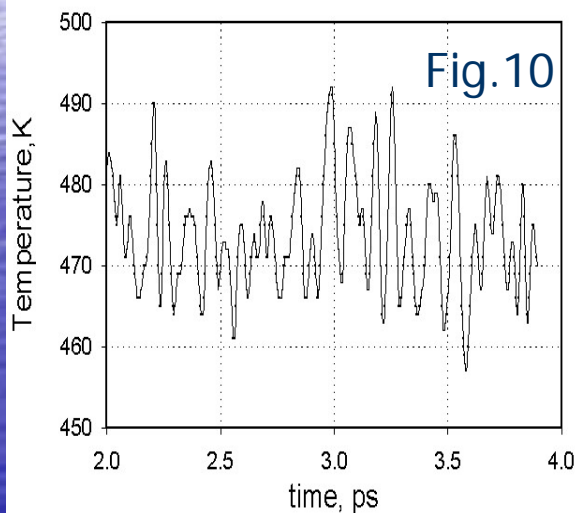Li ion positions at t/dt=10,000, density 0.52 g/cm3, T=453K

Fig.9

Fig.10

Fig.11

Liquid Lithium preparation:

We started from an ideal lattice (Fig.8), then it was melted (Fig.9) by heating at a high temperature for 30,000 time steps. After that the liquid was equilibrated for 10,000 time steps and then the physical variables were obtained: the system temperature (Fig.10), the radial distribution function (Fig.11), the velocity-autocorrelation function (vacf) (Fig.16), as an average for 20,000 time steps.

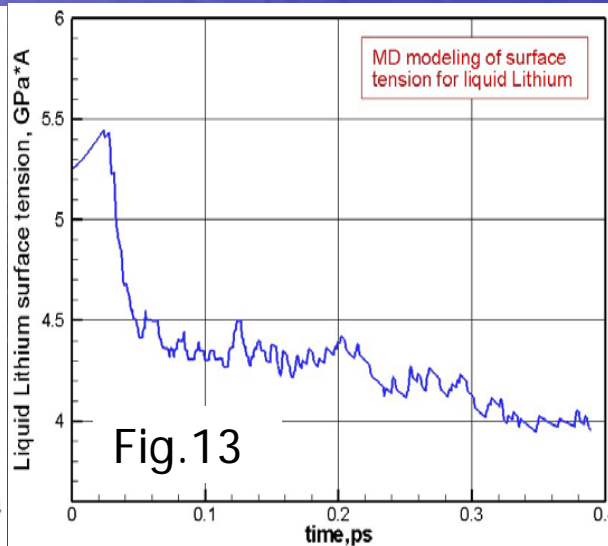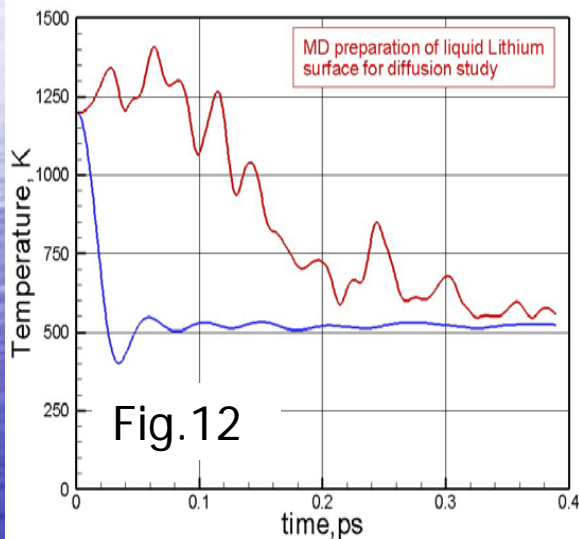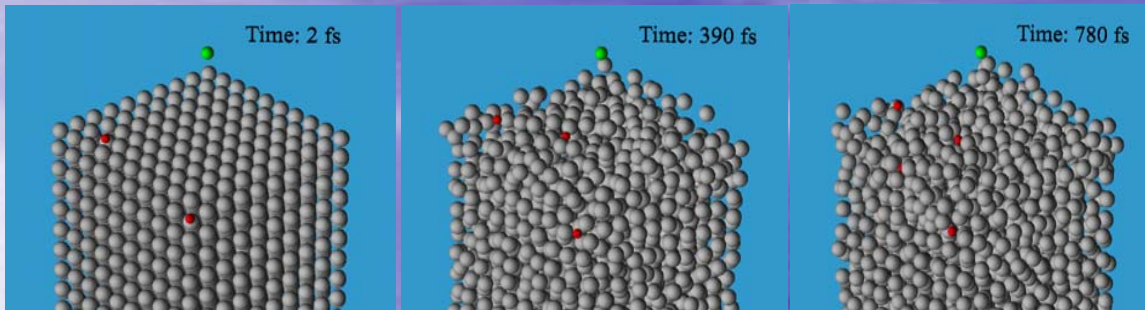# Preparation of liquid Lithium surface

Time: 2 fs   Time: 390 fs   Time: 780 fs

Time: 2 fs

Fig.14

MD preparation of liquid Lithium surface for diffusion study

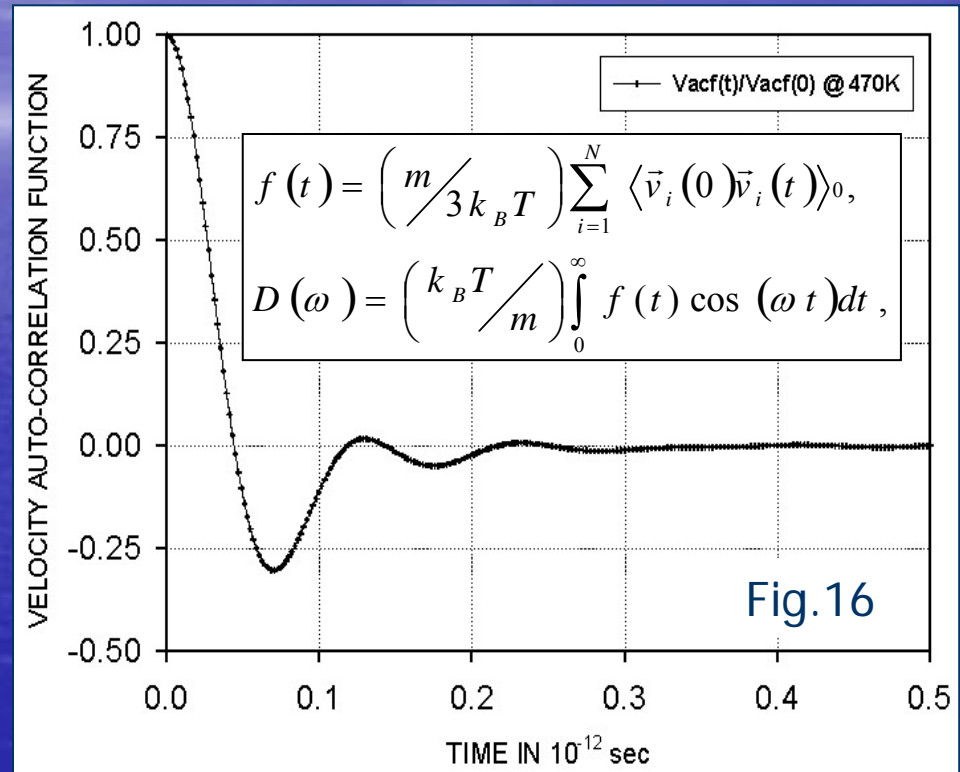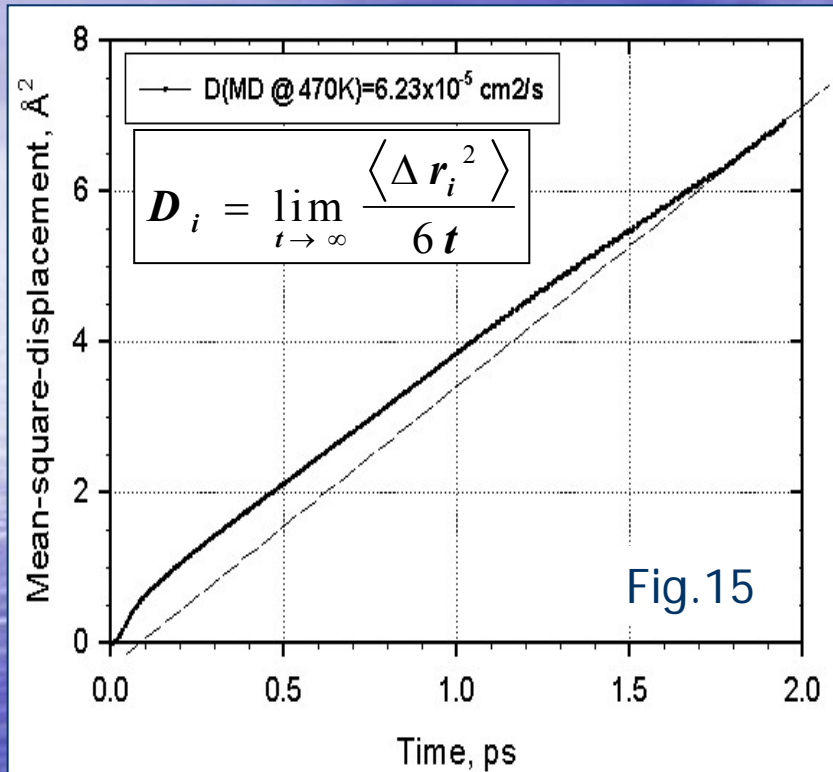Fig.12

MD modeling of surface tension for liquid Lithium

Fig.13
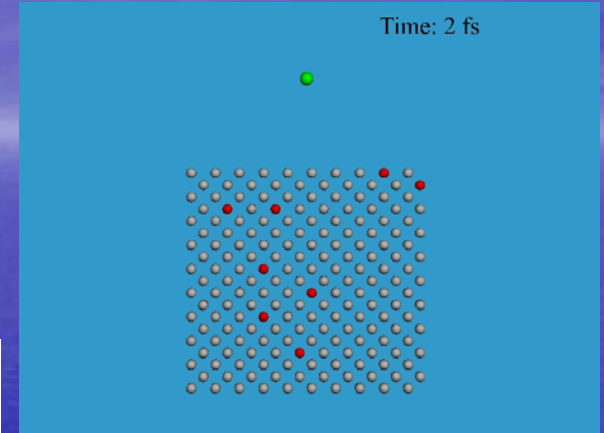
Important issues:

1) Temperature setting should not be used in the central area - for true particle dynamics and a correct sputtering Yield.
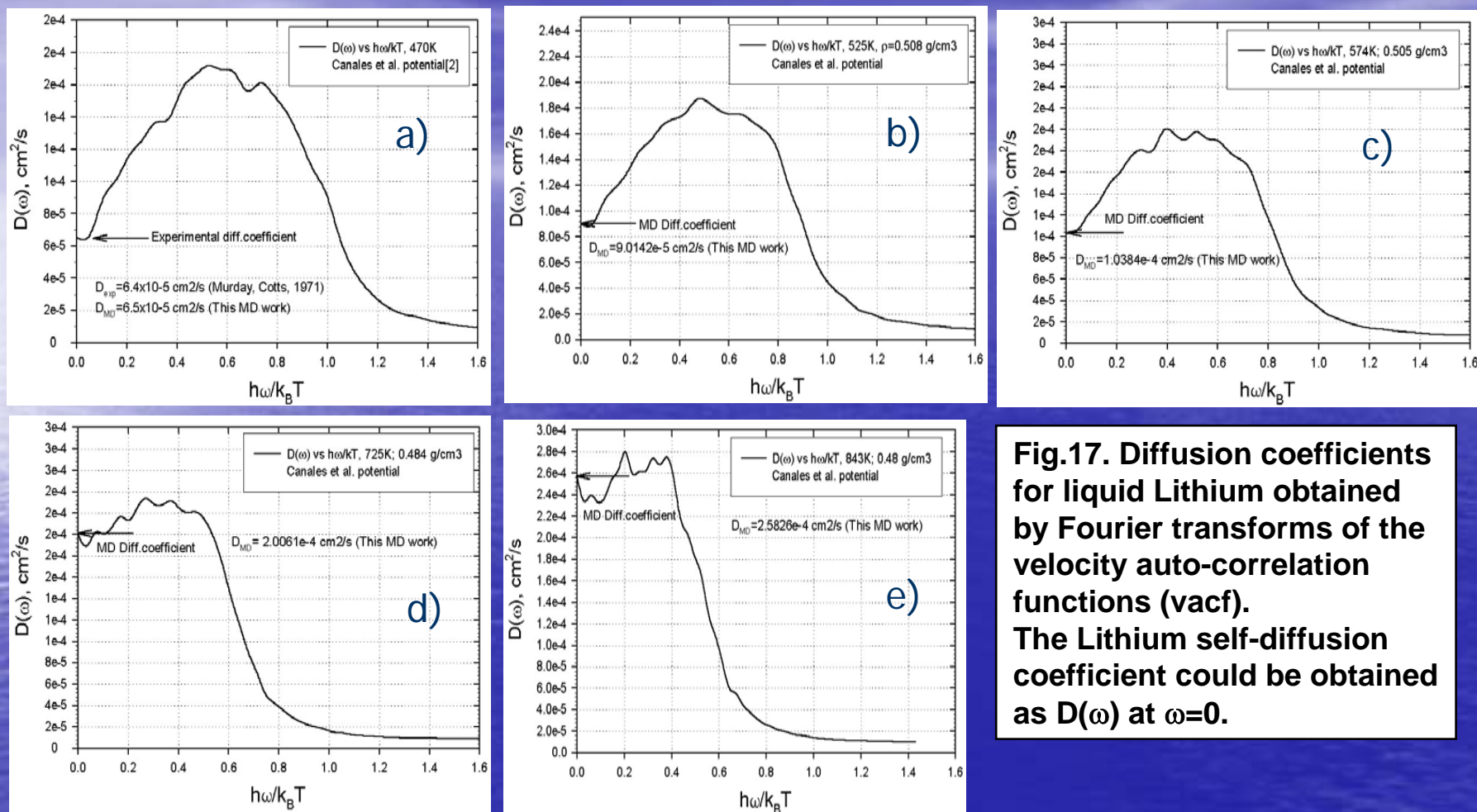2) The surface tension is controlled.

Diffusion coefficient by MD

Fig.15

$$D_i = \lim_{t \to \infty} \frac{\langle \Delta r_i^2 \rangle}{6t}$$

D(MD @ 470K)=6.23×10⁻⁵ cm2/s

Fig.16

Vacf(t)/Vacf(0) @ 470K

$$f(t) = \left(\frac{m}{3 k_B T} \right) \sum_{i=1}^{N} \langle \vec{v}_i(0) \vec{v}_i(t) \rangle_0 ,$$

$$D(\omega) = \left(\frac{k_B T}{m} \right) \int_0^{\infty} f(t) \cos(\omega t) dt ,$$

The Li self-diffusion coefficient was obtained by two methods: as a tangent of the ionic mean-square-displacements (Fig.15) and as a Fourier-transform of the vacf(t) (Fig.16).

Fourier transforms of Vacf

Fig.17. Diffusion coefficients for liquid Lithium obtained by Fourier transforms of the velocity auto-correlation functions (vacf).
The Lithium self-diffusion coefficient could be obtained as $D(\omega)$ at $\omega=0$.

The figures correspond to the data points at which there exist an inter-ionic potential:
a) T=470K, 0.513 g/cm3; b) T=525K, 0.508 g/cm3; c) T=574K, 0.505 g/cm3; d) T=725K, 0.484 g/cm3; e) T=843K, 0.48 g/cm3.

Trajectories of Li and He
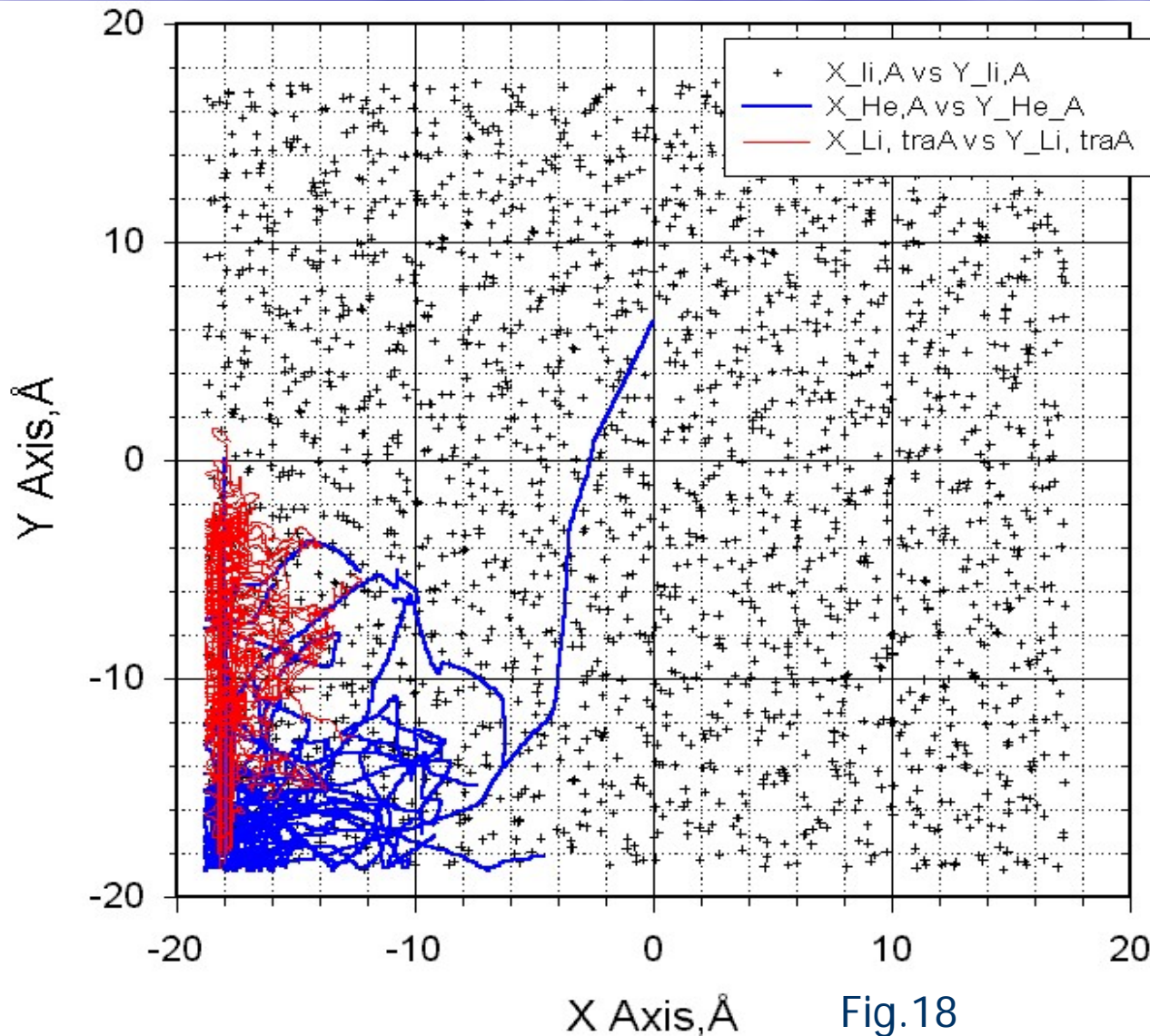
The red lines - trajectories for Lithium ions.

The blue lines - trajectories for Helium atoms.

Fig.18

Comparison with experiment

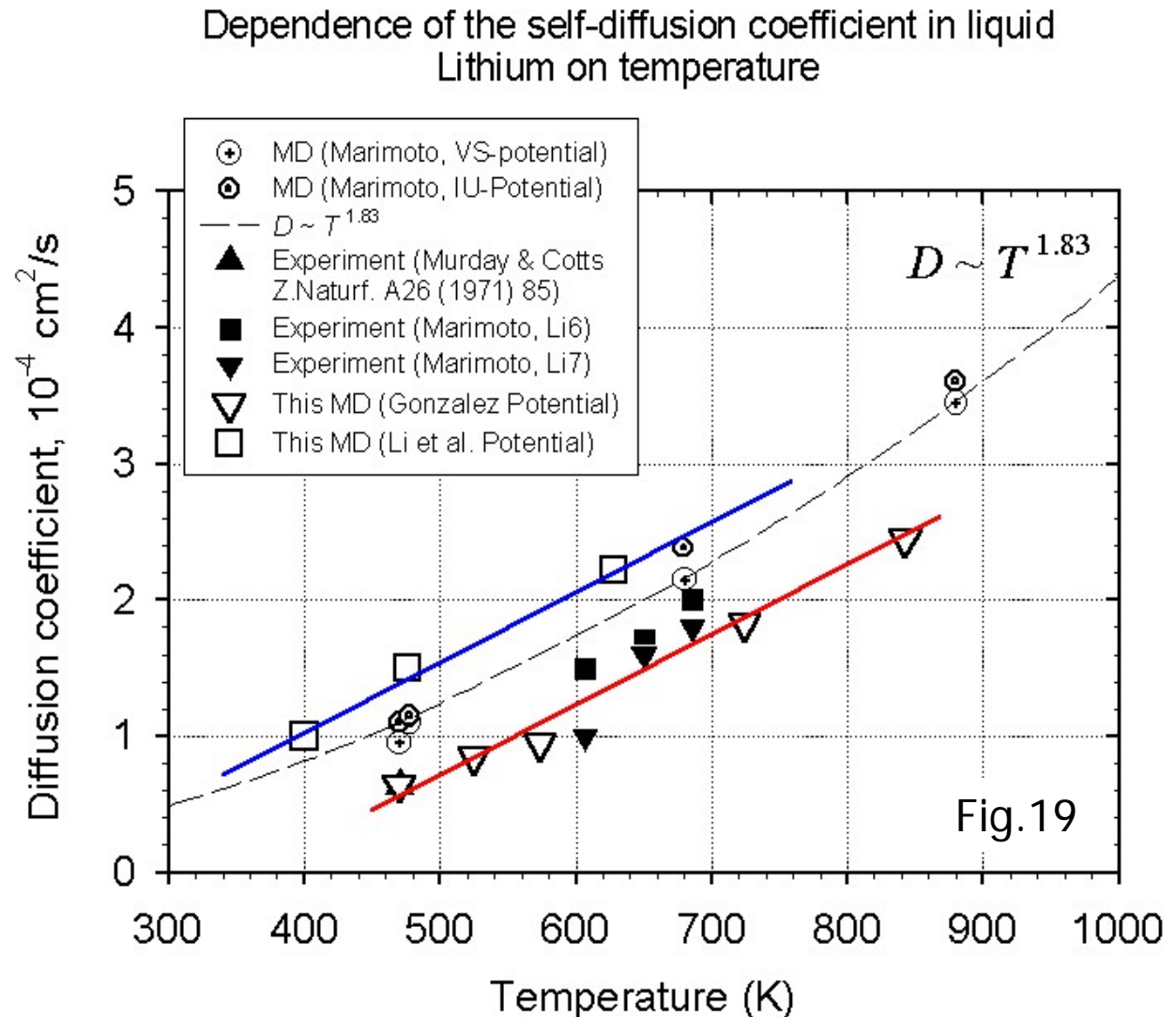The MD diffusion coefficients are compared with experiments.

The red line is drawn as "an eye guide" for potential [1].

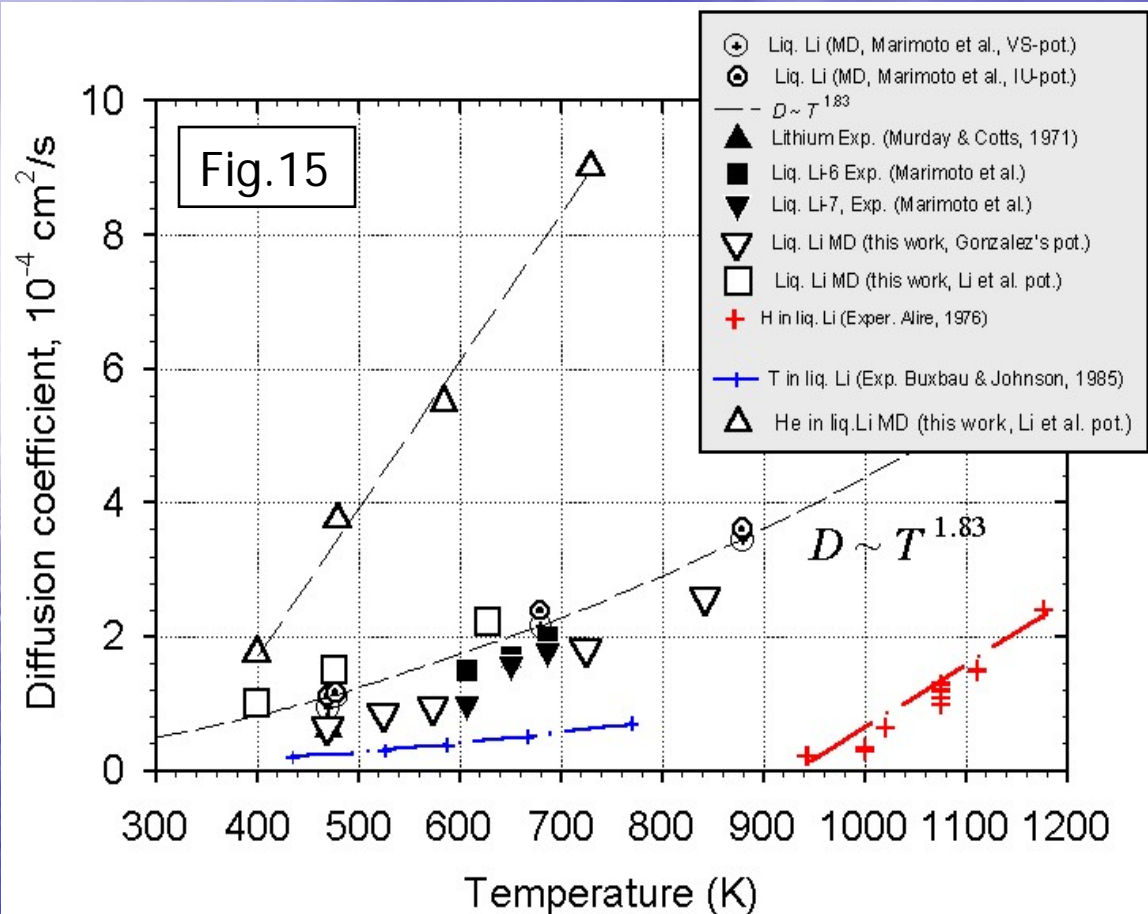The blue line – for the potential [2] (Li et al.).

References:
[1]. M. Canales et al, Phys. Rev.E50 (1994) p.3656.
[2]. Y. Li et al, Phys. Rev. B57 (1998) p.15519.

Dependence of the self-diffusion coefficient in liquid Lithium on temperature

$D \sim T^{1.83}$

Fig.19

Diffusion of He (MD) and H (exp.)

Fig.15

Legend:
- Liq. Li (MD, Marimoto et al., VS-pot.)
- Liq. Li (MD, Marimoto et al., IU-pot.)
- $D \sim T^{1.83}$
- Lithium Exp. (Murday & Cotts, 1971)
- Liq. Li-6 Exp. (Marimoto et al.)
- Liq. Li-7, Exp. (Marimoto et al.)
- Liq. Li MD (this work, Gonzalez's pot.)
- Liq. Li MD (this work, Li et al. pot.)
- H in liq. Li (Exper. Alire, 1976)
- T in liq. Li (Exp. Buxbau & Johnson, 1985)
- He in liq.Li MD (this work, Li et al. pot.)

$D \sim T^{1.83}$

Axis labels: Diffusion coefficient, 10^{-4} cm^2/s vs Temperature (K)

Summary:

- **MD results for the Diffusion constants obtained with two methods are in good agreement with available experimental data;**

- **Interatomic potential function is an important issue: the short range potentials change the energy barriers for diffusion.**

- **They give wrong diffusion constants and change the sputtering Yield.**

He/Li sputtering with He⁺ ions

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Time: 195 fs

Time: 390 fs

Time: 616 fs
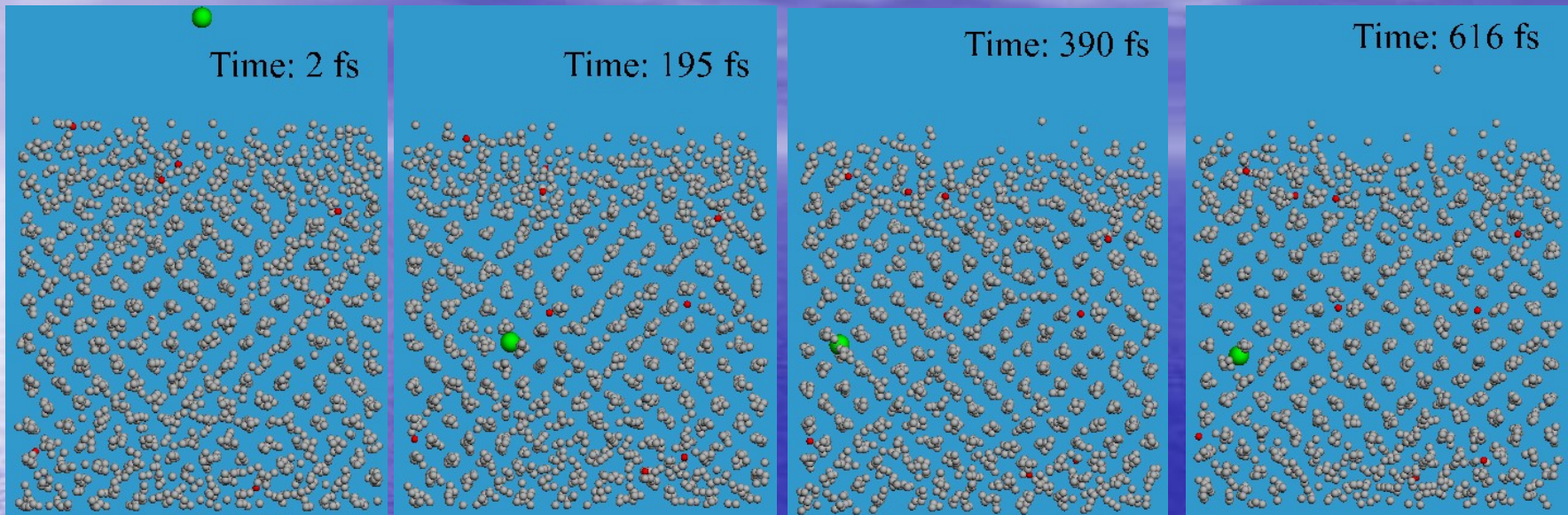
Comments for pure and He-saturated Li @ 470K:

- He⁺ ranges **may** decrease with the He content in Li – **this needs more analysis**;
- The analysis shows **more intense energy exchange** for the He saturated Li near the surface – **needs bigger system**;
- The Li sputtering Yield **could** increase with He content – **need more analysis**;
- Simulations are going on at higher temperatures for comparison

He+ interaction with liquid Lithium: He 0.5%

Ei=10eV
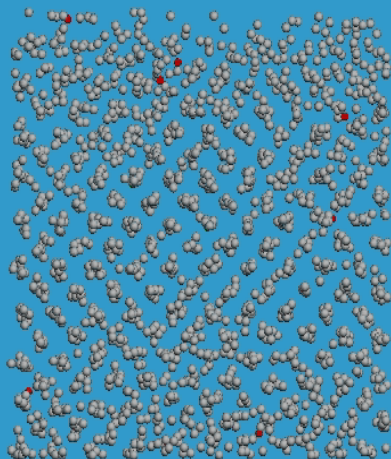
Ei=20eV
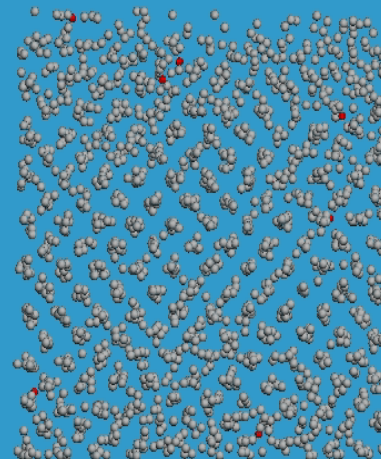
Time: 2 fs

Time: 2 fs

He$^+$ interaction with liquid Li: 0.5% vs 7% of He/Li content

Ei=50eV, 0.5% He/Li
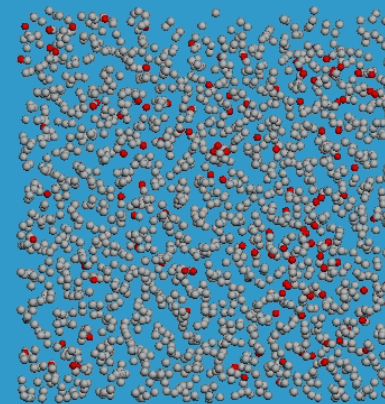
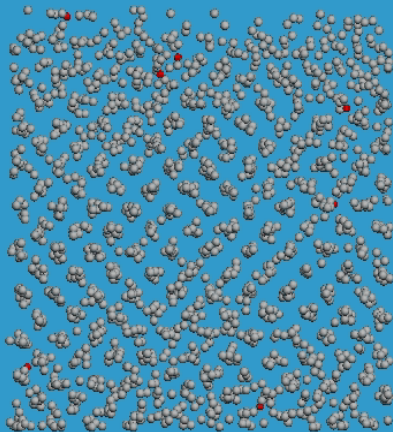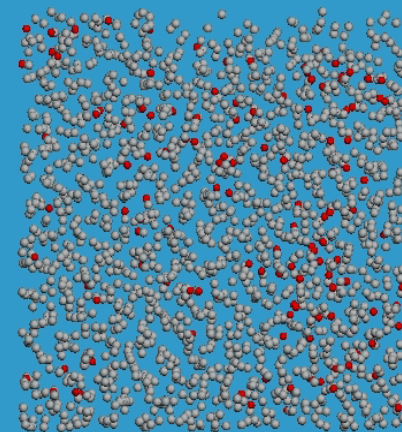Ei=50eV, 7% He/Li

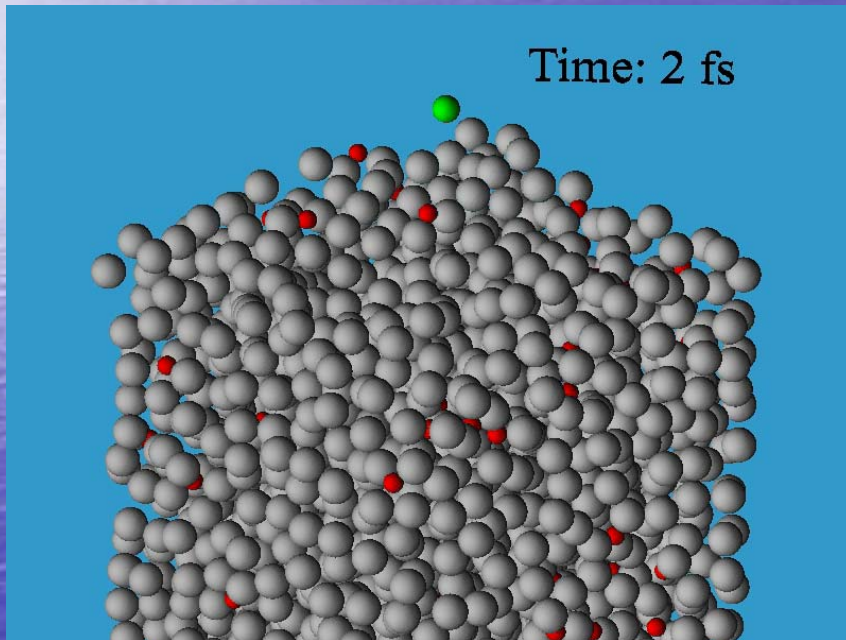# He+ interaction with liquid Lithium: He 0.5% vs 7%

Ei=80eV, 0.5% He/Li

Ei=80eV, 7% He/Li

He⁺ interaction with liquid Li: 7% of He in Li

Ei=10eV, 7% He/Li

Ei=20eV, 7% He/Li

Time: 2 fs

Time: 2 fs
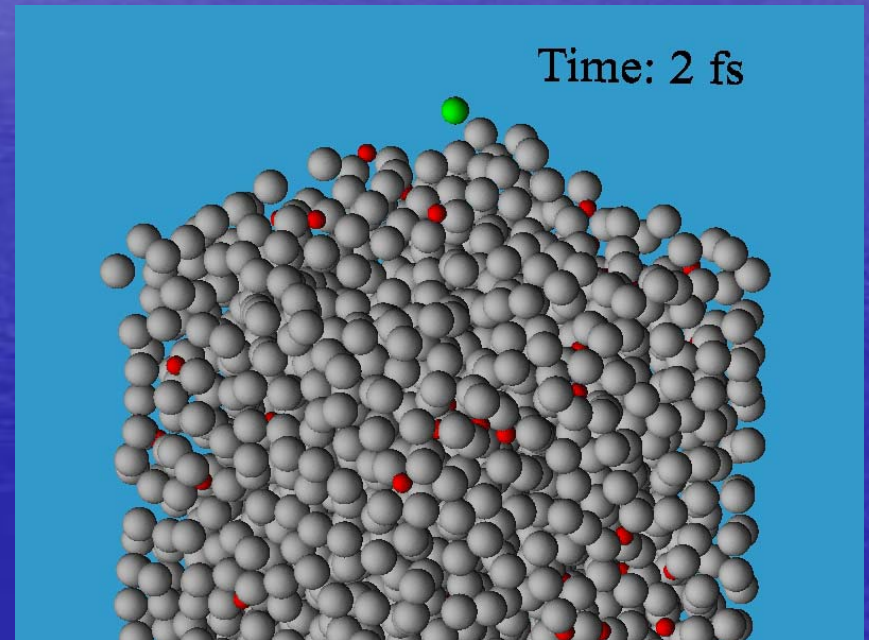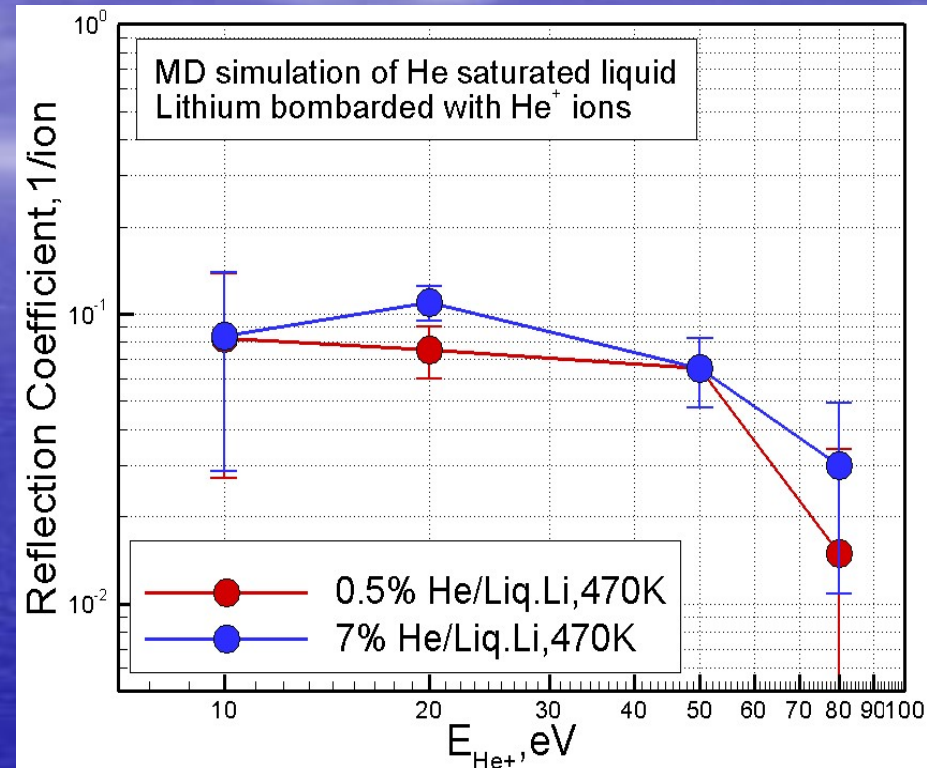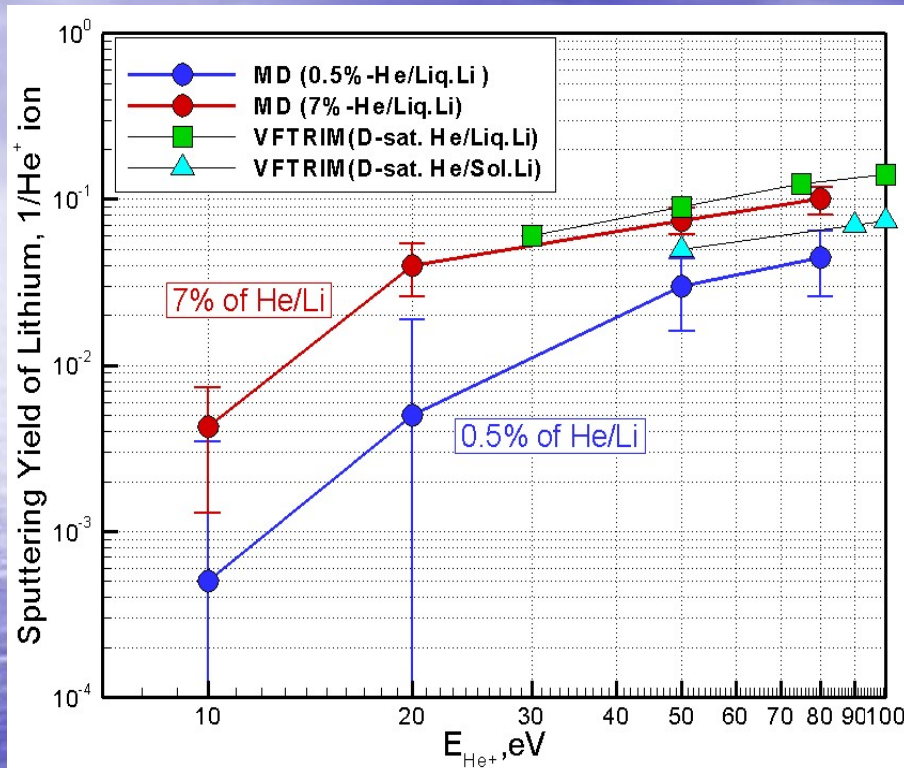
MD of He/Li sputtering with He⁺ ions

Comments:

- **MD takes into account the multiple collisions near the surface**;
- **No need for adjustment – however, the cut-off distances are important**;
- **Surface tension should be always compared to experimental data**;
- **Separation of thermal and knocked-out atoms is necessary.**

He bubbles in liquid Lithium

Motivation

The mechanisms of bubble formation in liquid metals are not well understood. They are important for liquid surface erosion under irradiation with He ions. There is a fundamental interest to this process [1].

Two processes, with different time scales:

1. Slow process – formation of a critical nucleus

MD will be used to calculate the binding energies and the kinetic coefficients. **This is a huge simulation task and will be performed in the future.** If the energies and kinetic coefficients are known, the rate equations or thermodynamic Saha equations solve the problem.

2. Fast process – Bubble collapse and sputtering

MD & MC simulations will be performed for collapse of a He bubble in liquid Li. PBC and a realistic Li-Li and He-Li potentials were used.

Thermodynamics of small bubbles

Bubble concentrations from mass action law (Saha equations)

$$A_2 \Leftrightarrow A + A$$
$$A_3 \Leftrightarrow A_2 + A$$
$$\ldots\ldots\ldots\ldots$$
$$A_k \Leftrightarrow A_{k-1} + A$$
$$\Sigma A_k = const\,(x, t)$$

$$\begin{cases} n_2 \Leftrightarrow 2n_1 \\ n_3 \Leftrightarrow n_2 + n_1 \\ n_k \Leftrightarrow n_{k-1} + n_1 \\ \sum_{k=1}^{N} k n_k = n_{av}(\phi_{He}, T_{Li}) \end{cases}$$

$$n_k = n_{k-1} n_1 \left(\frac{2\pi\hbar^2 k}{m_1 k_B T} \right)^{3/2} \frac{Q_k}{Q_{k-1} Q_1} \exp(\beta\varepsilon_k - \beta\varepsilon_{k-1}),$$
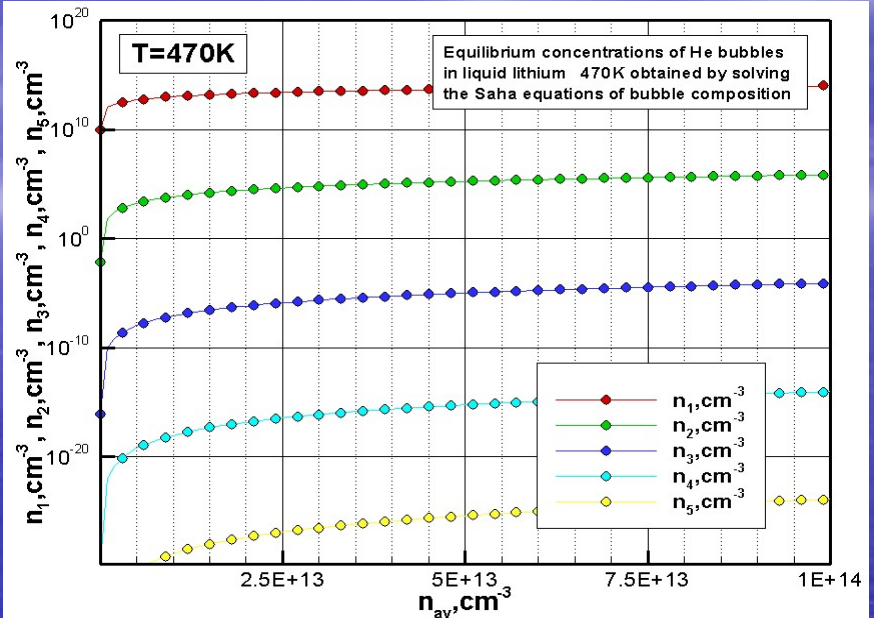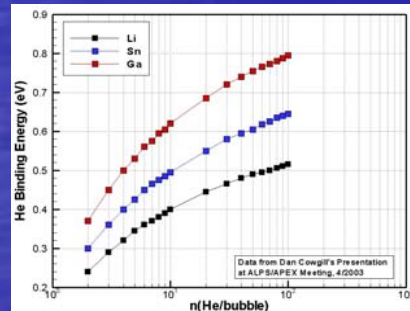
$$Q_k = \sum_k g_k \exp\left(-\frac{E_k}{k_B T} \right) - \text{internal partition functions,}$$

ε_k – the binding energies for the cluster of k - atoms,

g_k – degeneracy of energy levels,

m_1 – He atomic mass, $\beta = \dfrac{1}{k_B T}$

Metal	γ (GPa·Å)
Li	3.8
Sn	5.3
Ga	7.2

Data from Dan Cowgill's Presentation at ALPS/APEX Meeting, 4/2003

T=470K

Equilibrium concentrations of He bubbles in liquid lithium 470K obtained by solving the Saha equations of bubble composition

The parameters for this model are the binding energies E_k of He bubbles in liquid Lithium. Here we use the relation:

$$E_k = 4\pi\left[(r^2_{k-1} + r^2_1) - r^2_k\right]\gamma$$

G – the surface tension of liquid Lithium

Pros:
1) The equation are easy to solve
2) The binding energies are known for large clusters
3) For small clusters they could be found by MD, provided we know the potentials.

Contra:
1) They are equilibrium equations - do not give the stable macroscopic bubbles

Classical Nucleation Theory of Bubble formation

One-component system

$$F(R) = -\frac{4\pi}{3} R_b^{\,3} \Delta p + 4\pi\gamma R_b^{\,2},$$

$$R_{cr} = \frac{2\gamma}{\Delta p_{cr}} \Rightarrow W_{cr} = \frac{16\pi}{3}\frac{\gamma^3}{(\Delta p_{cr})^2},$$

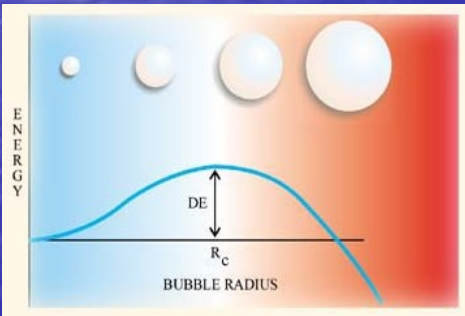$$J = J_0 \exp\left(-\frac{W_{cr}}{RT}\right), cm^{-3}s^{-1}$$

J_0 – is the kinetic factor

The Laplace equation :

$$p_{He} - p_{Li} = \frac{2\gamma}{R_b}, \; p_{He} = p_{Li} + \frac{2\gamma}{R_b}$$

$$\gamma_{Li} = 3.8\,GPa\text{Å}, \; R_b \sim 10\text{Å},$$

$$\Delta p \sim 0.76\,GPa$$

Binary-mixture: solvent - solute

$$W_{cr} \approx \frac{16\pi}{3}\frac{\gamma^3}{(\Delta p_{cr})^2},$$

$$J = J_0 \exp\left(-\frac{W_{cr}}{RT}\right), cm^{-3}s^{-1}$$

$$J_0 = \rho_{1s}\left(\frac{2\gamma_{lg}}{\pi}\right)^{1/2}\left[\frac{y_1}{m_1^{1/2}} + \frac{y_2}{m_2^{1/2}}\right],$$

ρ_{1s} – the number density of pure solvent, y_1 and y_2 – the vapor mole fractions of the solvent and the solute;

As stability of a bubble is defined by R_{cr} - if it is small, pressure in the solvent will be negative - the liquid is super-heated or stretched in V.

Potentials for low density Li are needed!

MD calculations for the He bubble formation in liquid Li

Bubble formation rate could be obtained by MD as the number of nuclei formed by the time $<\tau>$, in V.

$$J_{MD} = \frac{1}{<\tau>V}, \text{ where } V = N/n,$$

$$<\tau> - \text{ av. bubble form. time;}$$

$$W_{cr} = -kT \ln\left(J_{MD}/J_0\right)$$

The distribution function of small bubbles defines the minimum work W.

The obtained W gives the nucleation rate J_{MD}.

$$n_s/n_1 = \exp\left(-W_s/kT\right), \text{ therefore}$$

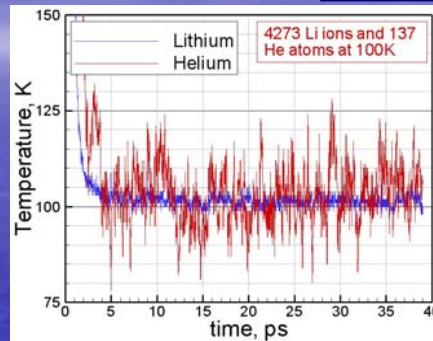$$W_{cr} = \lim_{s \to cr}\left(n_s/n_1\right), \text{ and then}$$

$$J_{MD}/J_0 = \exp\left(-W_{cr}/kT\right)$$

He bubble stability near the surface

T=600K
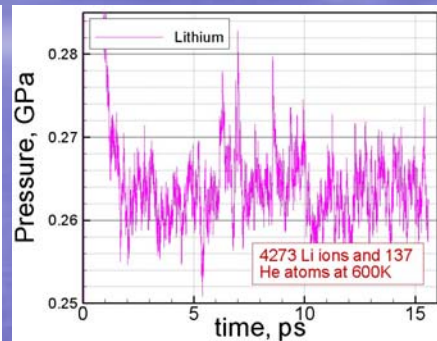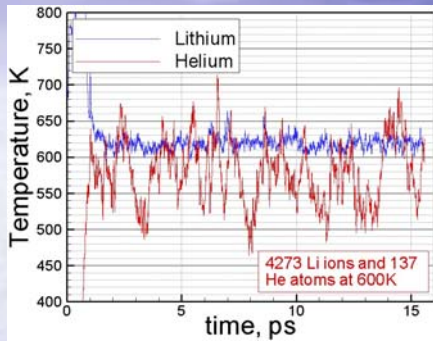
T=100K
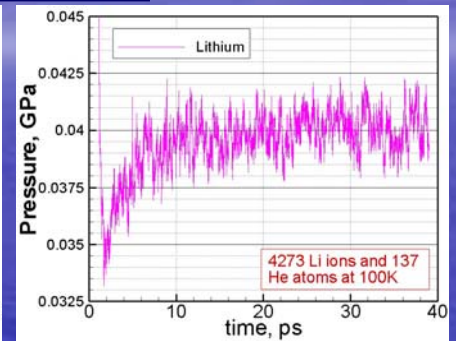
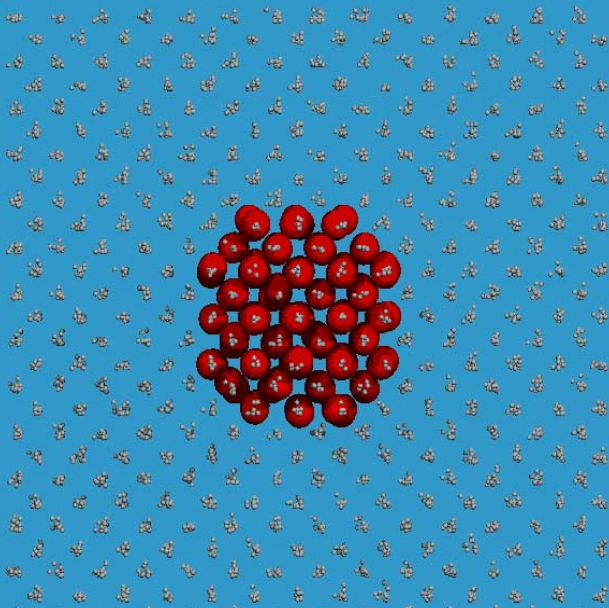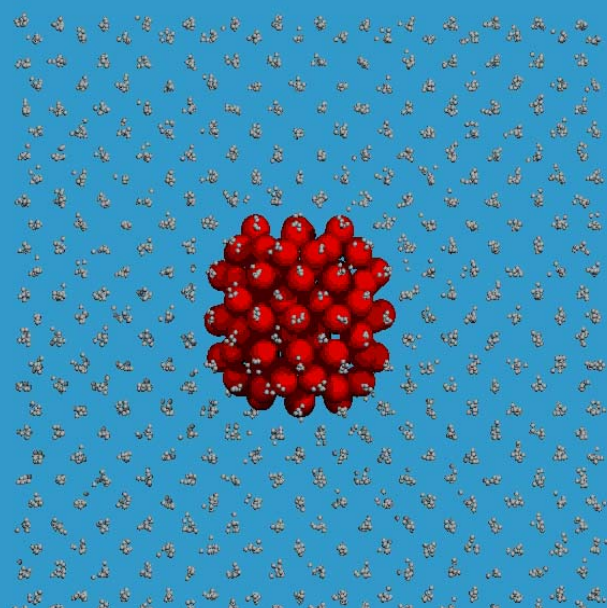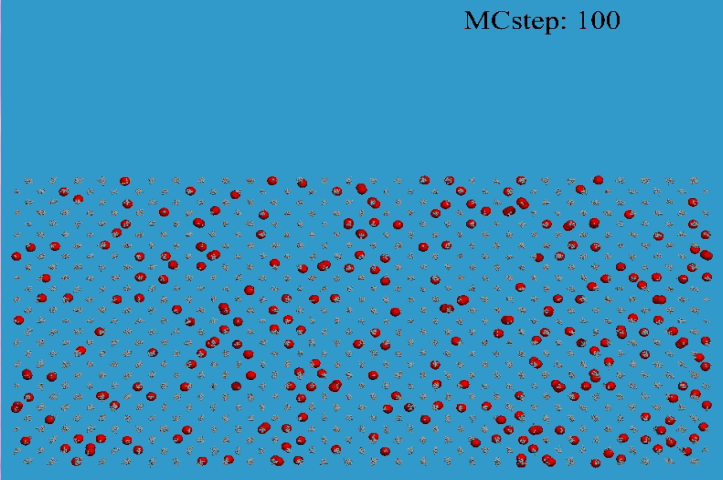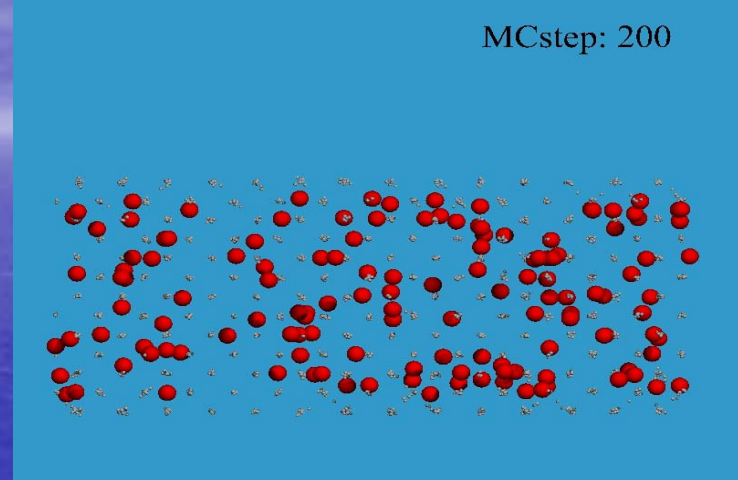# MC of He small He bubbles in Li


470K   MCstep: 100   MCstep: 200   47K

1. **He-bubbles could be obtained as the pairs that have space proximity (a geometry criterion) and negative relative total energies (an energy criterion) for all He atoms in the solution.**

2. **The He binding energies could also be found and then used in Saha equations.**

Conclusion for the direct MD & MC of He bubbles in Li:

- **Because the critical radius for a stable He bubble in liquid Li is macroscopically large (~ mm), the real bubble formation times are too far beyond of the scope of the conventional MD & MC methods;**

- **The newly developed Activation-Relaxation techniques may help to avoid the barriers and accelerate the simulation of He bubble formation.**

MD simulation of a fast process: bubble blast near the Lithium surface
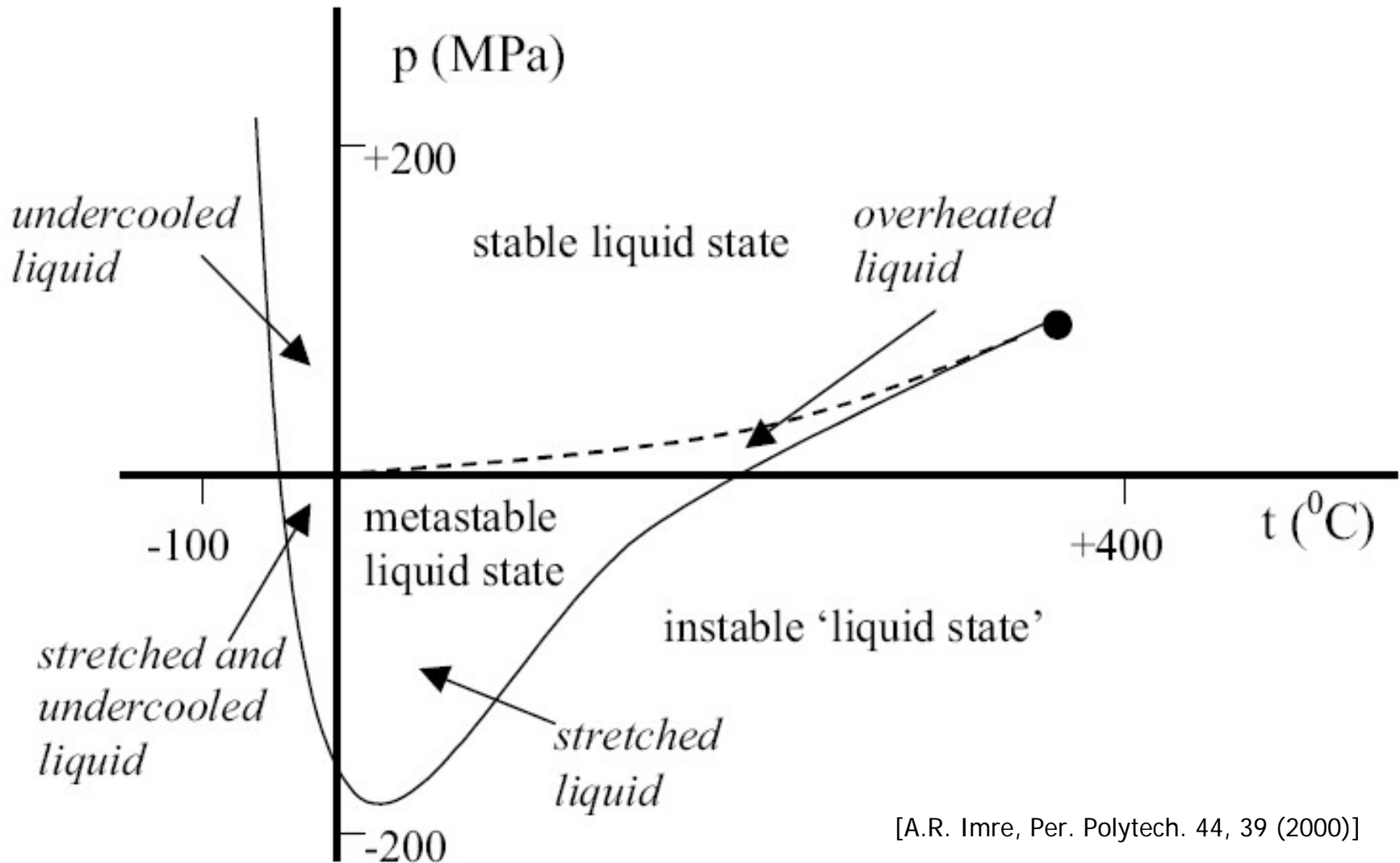

Time: 9 fs

Time: 4
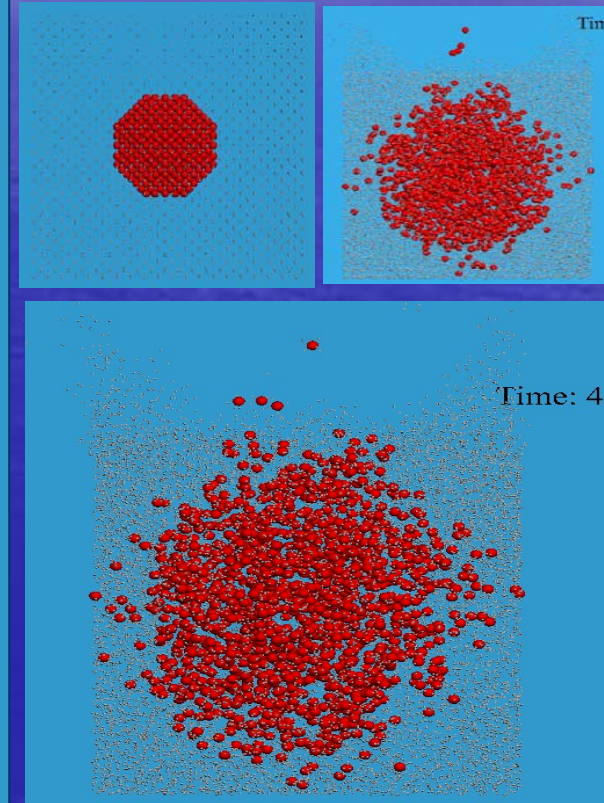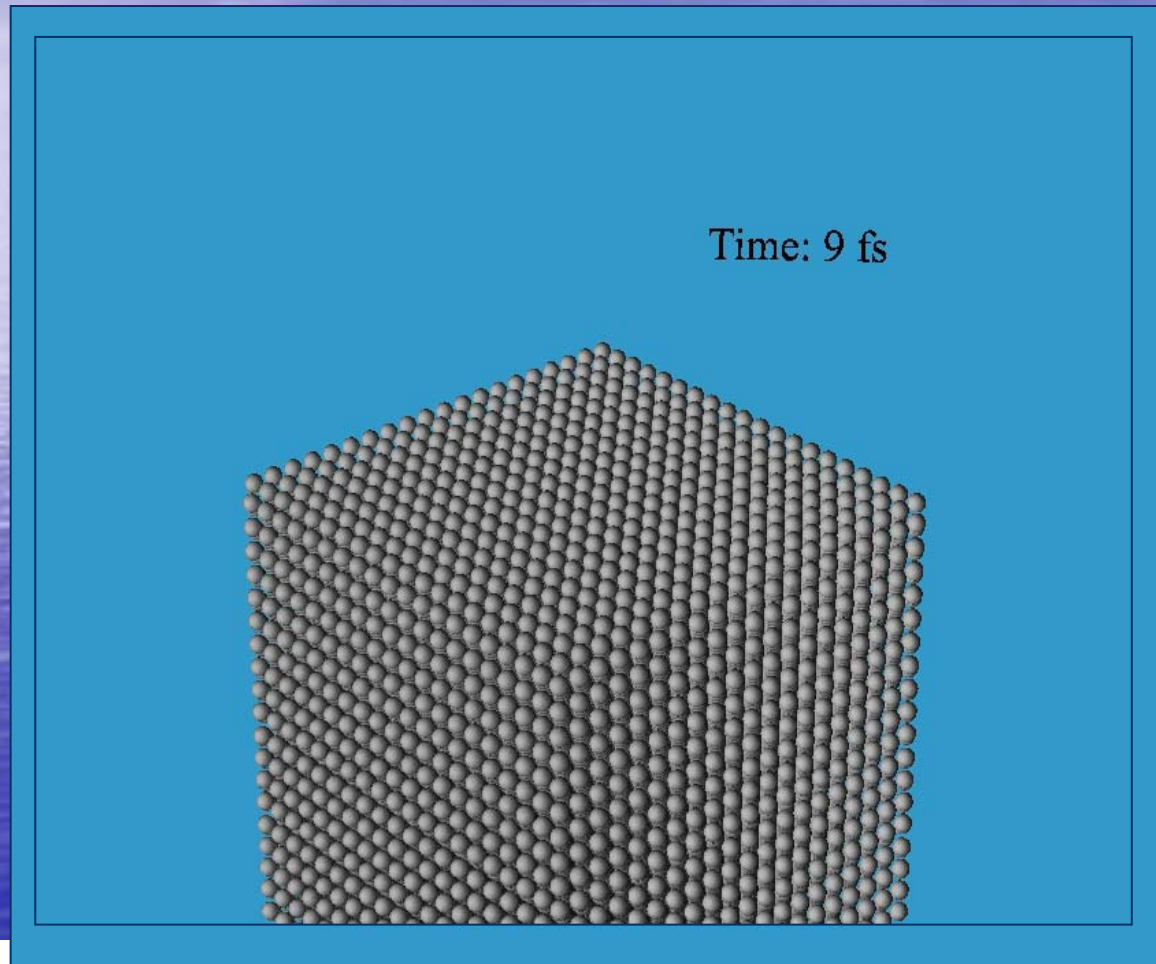
Summary

➢ Our extensive **MD** simulations of liquid Lithium show that **MD** has great capabilities for calculations of diffusion constants. Indeed, MD can do much more – together with the rate and Saha equations – it could be used to study a vast majority of the processes near the liquid Li and other metal surfaces. However, we need good potentials.

➢ Preliminary MD calculations of He/Li sputtering Yield bombarded with He+-ions with E<100eV have been carried out for liquid Li saturated with He and they show that **MD** is a convenient and a straightforward computational PMI method, without adjusting parameters.

➢ **MD** & **MC** methods has been used to study the kinetics of small He bubble formation and the dynamics of He bubbles near the liquid Li surface. **MD** could be used to shed the light at the most difficult problem in the theory of phase transition of binary liquids.

➢ Future study should be concentrated on the rate and Saha equation approaches -- a huge computational task of computing the kinetic coefficients and binding energies.

Phase diagram for water

[A.R. Imre, Per. Polytech. 44, 39 (2000)]